X-641-67-237

NASA TM X-55796

HAS THE EARTH'S CRUST CHANGED WITH TIME? RARE-EARTH ABUNDANCES IN ANCIENT SEDIMENTS

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MAY 1967

NASA

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GREENBELT, MARYLAND

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Possible changes in chemical composition of the earth's crust over the past several billions of years have been discussed in several recent papers. Engel[1] concluded that there has been a change in the composition of the North American crust during the last 3 billion (10^9) years, based primarily on increase with time of average sedimentary K/Na, Fe^{3+}/Fe^{2+} and Ca/Mg ratios. Condie[2], on the other hand, concluded from a study of major and trace element data on ancient graywackes that the North American crust has not changed appreciably in composition during the last 3.0 to 3.5 billion years. These speculations are part of a larger question concerning the growth of continents. Hurley and co-workers[3], on the basis of Sr isotopic studies, have concluded that there has been a continuous generation of primary sial from subsialic source regions over most of geologic time. In contrast, Patterson and Tatsumoto[4] interpreted their lead data as suggesting that the bulk of the North American continent was formed 3.5 to 2.5 billion years ago, and there has been little addition since that time.

With the expectation that further information on geochemically sensitive trace elements might help elucidate the general problem, we have analyzed for rare-earth elements in ancient sediments and compared their abundances to those in more recent sediments. Haskin and co-workers[5,6,7] have determined rare-earth abundances in a large number of sedimentary rocks and have arrived at the following conclusions: (1) The processes which are involved in the formation of the different types of sedimentary rocks (limestones, shales, sandstones, phosphates, etc.) cause no major differences in the relative abundances of the rare-earths. (2) The relative rare-earth abundances for separate, large, continental areas are the same, within experimental error. (3) The general sediment pattern exhibits, relative to the chondritic pattern, decreasing abundances of the light rare-earths from La to about Eu, and essentially the same relative abundances as in chondrites for the heavy rare-earths, from about Gd to Lu. The sediments analyzed by Haskin and co-workers were mainly Paleozoic or younger; it was noted, however, that three Precambrian sediments seemed to have somewhat anomalous rare-earth abundances and that this might reflect a greater heterogeneity of the earth's crust during its earlier development.[5]

We have analyzed for the seven even-atomic-number rare-earth elements plus europium (Eu) in five ancient sedimentary rocks, namely a Fig Tree shale, a Bulawayan limestone, two Birrimian phyllites and a Birrimian meta-graywacke. The analytical technique is mass-spectrometric stable-isotope dilution.[8] The Fig Tree shale, from the Swaziland System of southern Africa, has a minimum age of 3.0 b.y. by the Rb-Sr whole-rock isochron method (Allsopp, private communication). The Bulawayan system from Southern Rhodesia has a minimum age of 2.6 billion years.[9] The Birrimian sediments are from the vicinity of the Bosumtwi crater in Ghana; a Rb-Sr whole-rock isochron study of these and related sediments gives an age of about 2 b.y.[10,11]

The results of our rare-earth analyses are given in Table 1. The chondrite-normalized abundances are plotted in Figs. 1 and 2. Such normalization is common practice in the presentation of rare-earth data; it removes the even-odd effect of the Oddo-Harkins rule.[12,13] The chondrite values used to normalize our data were obtained by analysis of a composite of five of the chondrites previously analyzed by Schmitt et al.[14,15]; our values agreed to within 15% with the values reported by Schmitt and co-workers. The error bars shown in Figs. 1 and 2 represent only the internal precision of the analysis; they are plus and minus two standard deviations of the mean ($\bar{\sigma}$) of the number of determinations, each determination being calculated from two scans of the appropriate mass region. Also plotted in Figs. 1 and 2 are the rare-earth patterns of younger sediments from Haskin et al.[7] for which ages were given. All of these sediments, except for the Redfern limestone (Fig. 1, #2) and the Paluis shale (Fig. 2, #4), are Paleozoic to Recent in age, that is, 500-600 m.y. or younger. No designation other than Precambrian was given for the other two sediments. Rather than confuse the figure by showing all the data with accompanying errors, we have drawn the best simple curve through the data points. It is difficult to delineate the precise pattern for many of the rocks inasmuch as analytical errors, particularly for the heavy rare-earths, would seem to be quite large.

As shown in the figures, the sediments all have similar relative rare-earth abundances, although their absolute abundances differ by several orders of magnitude. The ancient sediments reported in this paper exhibit general rare-earth patterns similar to those of the younger sediments analyzed by Haskin and co-workers. The sizable Eu anomaly in the Bulawayan limestone pattern might seem to be an exception. However, Eu anomalies do occur in younger sediments, as shown by our analysis of the rare-earths in the Jurassic Solenhofen limestone (Fig. 1). These Eu anomalies might be due to the redox conditions operative during sedimentation. It appears, then, that sedimentary rocks have had much the same rare-earth patterns over the past 3 billion years.

The similarity in relative rare-earth abundances of most types of sedimentary rocks is most easily interpreted, as it was by Goldschmitt[16], in terms of most sediments having wide enough provenance that their relative rare-earth abundances are the same as the average abundances of the weathering crust. The oceanic rare-earth budget need not be considered because analyses of sea-water[17] show extremely low concentration of these elements. If the sedimentary pattern is assumed to be the same as that of the weathering crust, then the similarity of the rare-earth patterns for sediments dating back to 3 billion years indicates that the rare-earth abundances of the weathering crust, and, by extension, the nature of the weathering crust, have not changed appreciably during this time interval. This, in turn, implies either that the amount of material of the weathering crust has not appreciably changed over this period or that additions to the weathering crust (juvenile igneous rocks) are similar on the average to the material which composed the weathering crust 3 billion years ago, at least in as far as rare-earth abundances are concerned.

It is difficult to favor one of these alternatives over the other, inasmuch as the composition of the mantle and the processes leading to the formation of crustal material are obscure. The rare-earth abundances for the bulk earth are probably quite different from those of the crust. Stony meteorites have commonly been assumed to represent the bulk composition of the earth. Chondritic and the normal brecciated achondritic meteorites, in general, have the same relative abundances of the rare-earths.[14,15,18] In support of the meteoritic-bulk-earth model, a number of terrestrial rocks, including eclogites[19], peridotites[19], garnet peridotites, and andesites[20] have been found to have relative rare-earth abundances close to the meteoritic ones. In addition, some theoretical rare-earth models[21] of igneous differentiation imply the existence of terrestrial material with meteoritic rare-earth abundances. It seems likely, therefore, that the crustal rare-earth abundances are the result of igneous differentiation processes acting, perhaps in several steps, on material with the quite distinct meteoritic rare-earth abundances.

If the bulk composition of the earth is chondritic, and the crustal rare-earth abundances are the same as in shales, approximately 75% of the La and 10% of the Yb are in the crust.[19] Hence, in this model, the present mantle must be severely depleted in the lighter rare-earth elements. If the crust has grown continuously at a relatively constant rate over geologic time, younger mantle-derived rocks might be expected to show, on the average, lower relative abundances of the light rare-earths, and this should be reflected in the patterns of younger sediments. No such effect is observed. This would seem to indicate that the crust has changed little, either in composition or amount, over the last 3 billion years. However, in the chondritic model, if the rare-earths were concentrated in the source regions of crustal rocks rather than disseminated uniformly throughout the mantle, depletions of the light rare-earths with time would be less noticeable. Whether these depletions would be detectable depends upon the degree of rare-earth concentration in the source regions. For example, if these regions had rare-earth abundances similar to those of the calcium-rich achondritic meteorites, approximately ten times those in chondrites, the depletions in light rare-earths with time would not be detectable. Obviously, if the bulk composition of the earth is achondritic, changes in rare-earth patterns with time would also not be detectable even without enrichments in the source regions. Another consideration in these speculations is that the whole crust may not have rare-earth abundances similar to those in shales; rare-earth concentrations in a non-homogeneous crust might be expected to decrease with depth.[22] Thus, an unambiguous interpretation of the rare-earth data on ancient sediments is not possible at the present time.

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Table 1

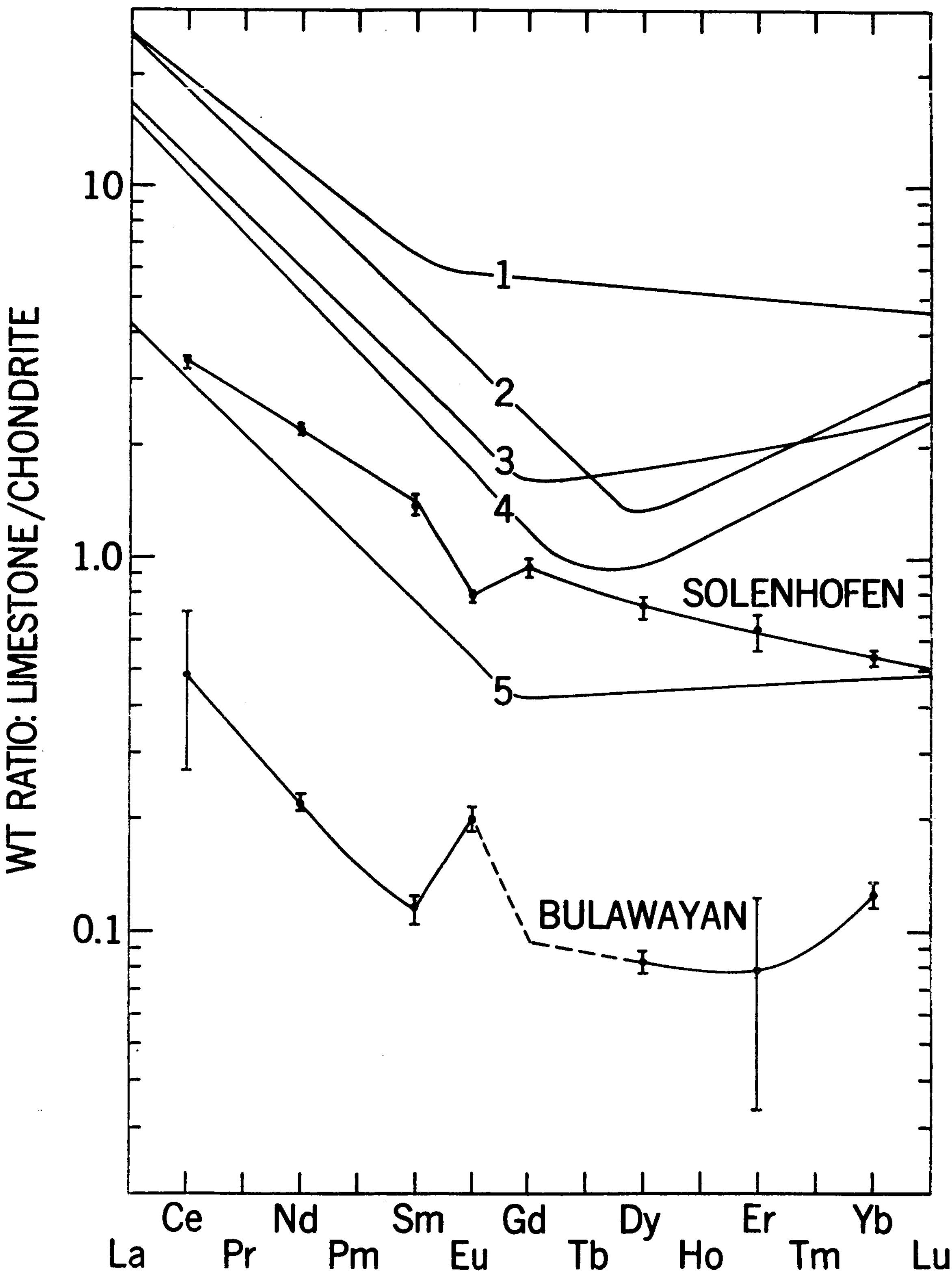
Rare-Earth Abundances, in ppm by weight

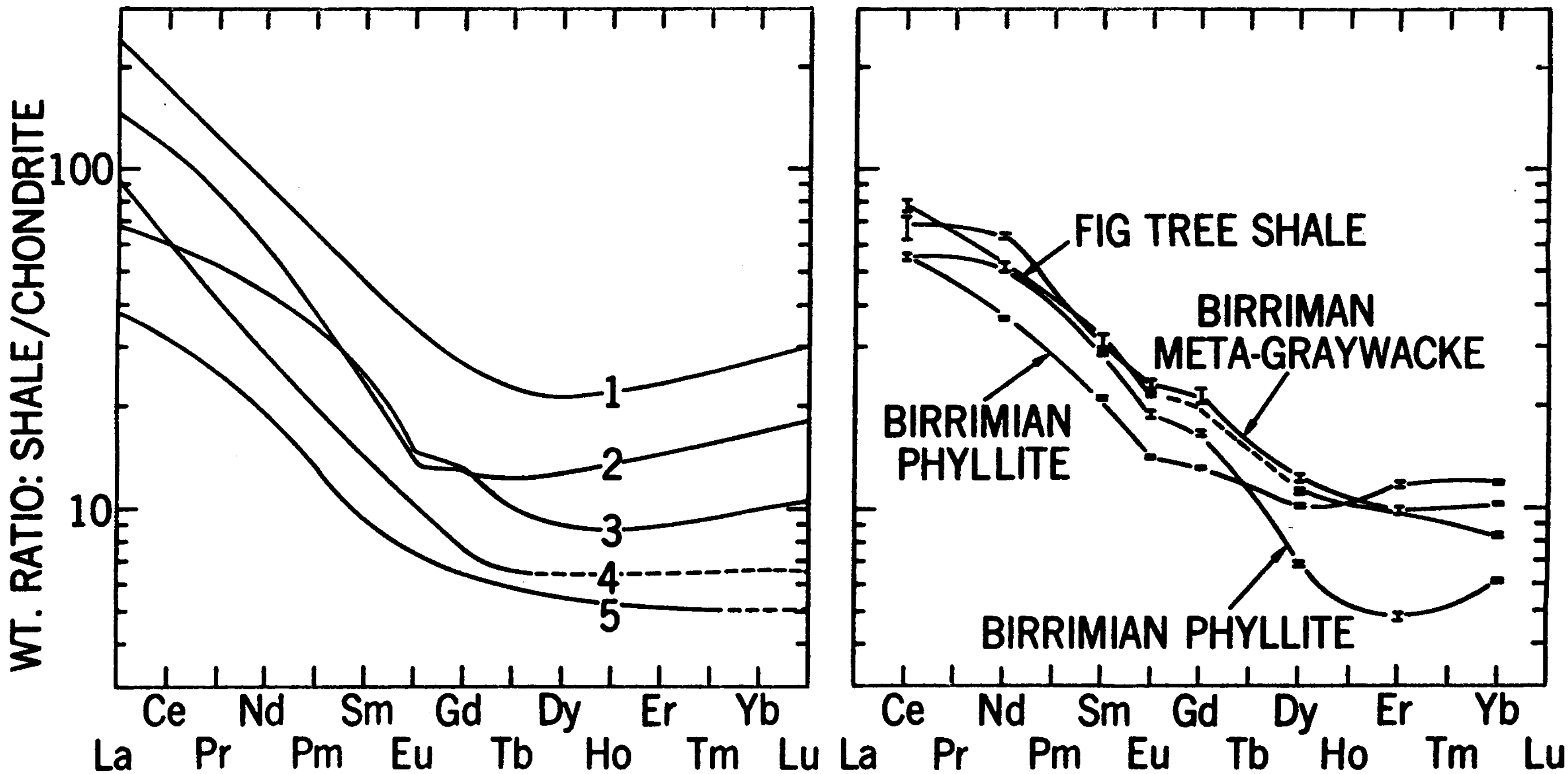
	Fig Tree Shale GSFC #60B	Birrimian Phyllite MIT #R5956	Birrimian Phyllite GSFC #159	Birrimian Meta-Graywacke MIT #R5959	Bulawayan Limestone GSFC #33	Solenhofen Limestone GSFC #44
Ce	61.8±1.1	45.2±1.3	43.0±0.4	53.6±2.1	0.39±0.9	2.61±0.01
Nd	$33.9_8 \pm 0.0_6$	33.6±0.1	$23.6_6 \pm 0.0_4$	41.7±0.1	0.145±0.004	$1.42_7 \pm 0.00_4$
Sm	6.70±0.02	5.96±0.05	4.43±0.01	6.70±0.21	0.024±0.001	0.280±0.001
Eu	1.54±0.01	1.35±0.01	0.993±0.003	1.66±0.02	$0.014 \pm 0.000_6$	0.057±0.000
Gd	-	4.28±0.02	3.31±0.01	5.49±0.13	-	0.242±0.001
Dy	3.38±0.02	2.06±0.02	$3.07_0 \pm 0.00_6$	3.72±0.04	$0.025_2 \pm 0.000_9$	0.223±0.001
Er	1.78±0.01	0.87±0.01	2.12±0.01	1.77±0.04	0.014±0.004	0.118±0.001
Yb	$1.90_7 \pm 0.00_5$	$1.14_2 \pm 0.00_6$	$2.28_9 \pm 0.00_5$	1.56±0.01	0.024±0.001	0.104±0.001

Figure Captions

Figure 1 Chondrite-normalized rare-earth abundances in limestones. Patterns with numbers are from Haskin *et al.*[5]: #1 Cleeve Hill oolitic ls. (Jurassic), #2 Redfern Lake ls. (Precamb.), #3 Leavenworth ls. (Penn.), #4 Florida Keys carbonate (Recent), #5 Byron fm. ls. (Silurian).

Figure 2 Chondrite-normalized rare-earth abundances in shales. Patterns with numbers (in Fig. 2A) are from Haskin *et al.*[5]: #1 Muncie Creek shale (Penn.), #2 Trenton shale (Ord.), #3 Moyers shale (Miss.), #4 Paluis shale (Precamb.), #5 Sillery shale (Paleozoic).


WT RATIO: LIMESTONE/CHONDRITE
10
1.0
0.1
1
2
3
4
5
SOLENHOFEN
BULAWAYAN
Ce
Nd
Sm
Gd
Dy
Er
Yb
La
Pr
Pm
Eu
Tb
Ho
Tm
Lu



WT. RATIO: SHALE/CHONDRITE
100
10
1
2
3
4
5
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
FIG TREE SHALE
BIRRIMAN
META-GRAYWACKE
BIRRIMIAN
PHYLLITE
BIRRIMIAN PHYLLITE
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu